

Phase equilibria in the system nitrogen-ethane and their prediction using cubic equations of state with different types of mixing rules

Gabriele Raabe* and Jürgen Köhler

Institut für Thermodynamik, Technische Universität Braunschweig

Hans-Sommer-Str. 5, 38106 Braunschweig, Germany

Abstract

The system nitrogen-ethane is of fundamental importance for the examination of nitrogen-alkane systems that exhibit miscibility gaps. The aim of this work is to compare the widely used SRK and PR cubic equation of state with different types of mixing rules with respect to their ability to represent the phase behaviour of this system. We investigated the performance of the van der Waals mixing rule, two composition depending mixing rules and some G^E -mixing rules in combination with the NRTL and UNIQUAC model. The binary interaction parameters were obtained by fitting only experimental VLE data and then used to test the capability of the different mixing rules to predict the VLLE and to describe the saturation densities. New experimental results for the VLE below 140 K including densities supplement available data sets needed to validate the correlation results.

Keywords: data, vapor-liquid-(liquid)-equilibrium, equation of state, mixing rules

*** corresponding author**

1. Introduction

Ethane is the first alkane that exhibits miscibility gaps in mixtures with nitrogen. Thus, the system nitrogen-ethane is of fundamental importance for the examination of this phase behaviour – in particular with regard to the description of natural gas systems.

Due to their simplicity, cubic equations of state (CEOS) from Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR) with the van der Waals mixing rule are the most frequently used models in the design of natural gas processes. But these models yield poor results for the prediction of the low temperature phase behaviour of nitrogen-alkane mixtures, when these systems exhibit miscibility gaps and vapor-liquid-liquid phase equilibria (VLLE). The shortcoming of the equations is mostly based on the lack of flexibility of the simple mixing rule.

In general a large number of mixing rules has been proposed to extend the use of CEOS to a wide range of conditions. Solórzano-Zavala et al. [1] pointed out some essential features of convenient mixing rules. These include the capability to predict equally well VLE of binary and multi-component mixtures of non-polar and highly non-ideal mixtures but also the prediction of vapor-liquid-liquid equilibria and other properties. The investigation of the performance of different mixing rules has been concentrated on studies of the representation of multi-component VLE data [1-3]. In contrast, only little attention was paid to the simultaneous prediction of VLE and VLLE phase behaviour, in particular for systems like nitrogen-alkane mixtures that exhibit miscibility gaps in the low temperature range. This is understandable in view of the fact that accurate experimental data to validate the correlation results are scarce. For the same reason also the influence of the mixing rule on the description of the saturation densities has not really been investigated in depth.

Therefore we supplemented reported data for the system nitrogen-ethane [4–17] by new experimental results for the VLE at low temperatures ($T \leq 140$ K) including saturated densities. All data were then used to compare the SRK and PR equations of state with different types of mixing rules with respect to their ability to represent the VLE and VLLE in the system nitrogen-ethane including saturation densities. The study covers the classical van der Waals mixing rule, two composition depending mixing rules and some G^E -mixing rules combined with the NRTL and UNIQUAC model. The binary interaction parameters were adjusted to the experimental VLE data only. These parameters were then used to test the capability of the mixing rules to predict the VLLE and to investigate their influence on the description of saturation densities.

2. Experimental section

The experimental study of the system nitrogen-ethane was carried out in an apparatus with recirculation loops for all equilibrium phases which has been described in detail in an earlier paper [14]. The experimental uncertainties of the temperature, composition and pressure measurements are $\Delta T = \pm 5$ mK, $\Delta x = \pm 0.005$ mol/mol and $\Delta p = \pm 8$ hPa for pressures less than 3.5 MPa. The uncertainties of the density measurements are estimated to be $\Delta \rho' / \rho' = 0.75\%$ and $\Delta \rho'' / \rho'' = 0.55\%$. The phase equilibria measurements for the system nitrogen-ethane in the temperature range 115-140 K are listed in Table 1-3. The new experimental data were compared with data from literature where such data

already existed. Fig. 1 illustrates the good agreement with published data [12,13] and shows that our data are usefully supplementing and expanding them.

Table 1: Experimental pTx-data of the VLE in the system nitrogen-ethane

T (K)	p (MPa)	x'_{N_2} (mol/mol)	x''_{N_2} (mol/mol)
119.9114	0.9732	0.0882	0.9965
119.7543	1.4487	0.1393	0.9980
119.8202	1.5896	0.1598	0.9976
119.9192	1.8004	0.1886	0.9983
119.8003	1.9783	0.2180	0.9982
124.9542	1.2881	0.1006	0.9969
124.9965	1.4966	0.1177	0.9989
124.9831	1.8710	0.1602	0.9978
129.3511	0.8630	0.0623	0.9988
129.5642	1.2128	0.0864	0.9980
129.6934	1.3178	0.0961	0.9976
129.8626	1.5057	0.1097	0.9967
129.6780	1.5145	0.1144	0.9983
129.9133	1.6641	0.1198	0.9985
129.9313	1.7355	0.1300	0.9987
129.3577	2.0863	0.1561	0.9968
129.7285	2.6711	0.2065	0.9987
129.8095	2.6939	0.2091	0.9990
130.0623	3.2804	0.2666	0.9984
138.3978	0.8787	0.0499	0.9936
138.3978	2.4852	0.1484	0.9954

Table 2: Experimental ρ' -data of the VLE in the system nitrogen-ethane

T (K)	p (MPa)	x'_{N_2} (mol/mol)	ρ' (mol/l)
119.9114	0.9732	0.0882	21.0439
119.9029	2.3378	0.2713	21.7811
124.8781	0.6059	0.0441	20.6683
124.9965	1.4966	0.1177	21.1066
124.8961	2.6700	0.2585	21.8499
129.9310	2.7545	0.2129	21.1835
138.3978	2.4852	0.1484	20.5044

Table 3: Experimental ρ'' -data of the VLE in the system nitrogen-ethane

T (K)	p (MPa)	x''_{N_2} (mol/mol)	ρ'' (mol/l)
114.9890	0.7146	0.9983	0.8084
119.9959	0.8815	0.9957	0.9596
119.9114	0.9732	0.9965	1.0790
119.7543	1.4487	0.9980	1.7557
119.8202	1.5896	0.9976	2.0429
119.8003	1.9783	0.9982	2.7847
124.9542	1.2881	0.9969	1.4367
124.9965	1.4966	0.9989	1.6843
124.9146	1.5341	0.9986	1.7748
124.9831	1.8710	0.9978	2.2788
129.9915	0.7481	0.9952	0.7140
129.3511	0.8630	0.9988	0.8437
129.8626	1.5057	0.9967	1.6552
129.6780	1.5145	0.9983	1.6631
129.9193	1.6641	0.9985	1.8627
129.9313	1.7355	0.9987	1.9713
130.0479	2.1827	0.9987	2.6280
129.6880	2.6542	0.9989	3.5790
130.0623	3.2804	0.9984	5.2925
138.8912	0.8787	0.9936	0.8059

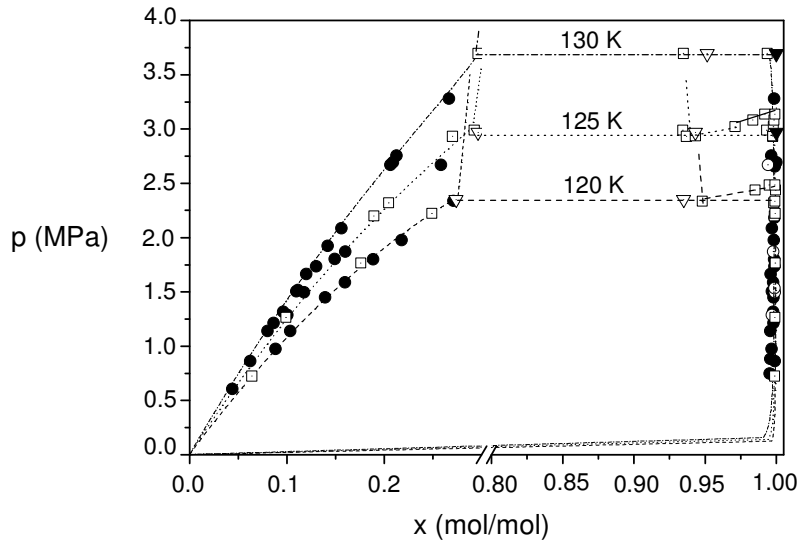


Fig. 1: Comparison of experimental results for the system nitrogen-ethane:
 ● this work, □ Kremer [12] and ▽ Llave et al. [13]

3. Thermodynamic models

The general expression of a cubic equation of state is given by

$$p = \frac{RT}{v-b} - \frac{a}{(v+\delta_1 b)(v+\delta_2 b)} \quad (1)$$

with $\delta_1 = 1$, $\delta_2 = 0$ for the SRK and $\delta_1 = 1 + \sqrt{2}$, $\delta_2 = 1 - \sqrt{2}$ for the PR equation of state. Most commonly used is the van der Waals mixing rule with just one interaction parameter k_{ij} in the expression for the parameter a (vdW1).

$$a = \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{ij}), \quad b = \sum x_i b_i \quad (2)$$

Shibata and Sandler [18] pointed out that a second interaction parameter in the mixing rule for b (vdW2) can lead to better results for many mixtures.

$$a = \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{ij}), \quad b = \sum \sum x_i x_j \left(\frac{b_i + b_j}{2} \right) (1 - d_{ij}) \quad (3)$$

To achieve a higher flexibility of the mixing model, several authors proposed modified versions of the classical vdW1 mixing rule that use composition dependent binary interaction parameters. As examples we choose the MKP mixing rule from Mathias et al. [19] because it does not suffer from the Michelsen-Kistenmacher syndrome

$$a = \sum \sum x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) + \sum x_i \left[\sum x_j (a_i a_j)^{1/6} (k_{ij} - k_{ji})^{1/3} \right]^3. \quad (4)$$

and the TBCC mixing rule proposed by Twu et al. [20] with an additional temperature dependency on the interaction parameter.

$$a = \sum \sum x_i x_j \sqrt{a_i a_j} \left(1 - \frac{k_{ij}}{T} \right) - \sum x_i \frac{\left[\sum x_j (a_i a_j)^{1/6} H_{ij}^{1/3} G_{ij}^{1/3} \right]^3}{\sum x_j G_{ij}} \quad (5)$$

$$H_{ij} = \frac{(k_{ij} - k_{ji})}{T}, \quad G_{ij} = \exp(-\beta_{ij} H_{ij}).$$

For both models as well as for the following ones the mixing rule for b is given by Eq. (2). Another approach to describe complex phase behaviour are G^E -mixing rules that incorporate an activity coefficient model (ACM) into the EOS model by equating the excess Gibbs energy G^E or the excess Helmholtz energy A^E calculated from the two models. The different G^E -mixing rules differ in the conditions of this equating and the related assumptions made to simplify the resulting mixing rule. As examples we investigated the HVOS and CHV mixing rules proposed by Orbey and Sandler [21,22], the MHV1 model by Michelsen [23], the PSRK mixing rule from Fischer [24] and the LCVm mixing rule from Boukouvalas et al [25]. The HVOS mixing rule [21] equates A^E modelled by an activity coefficient model and by the CEOS at infinitive pressure

$$\frac{a}{bRT} = \sum x_i \frac{a_i}{b_i RT} + \frac{1}{C} \sum x_i \ln \frac{b}{b_i} + \frac{A_\infty^E}{CRT}. \quad (6)$$

The function C , also used in all following G^E -mixing rules, depends on the CEOS chosen and the ratio u of the molar volume and the close-packing parameter b

$$C = \frac{\ln\left(\frac{u + \delta_2}{u + \delta_1}\right)}{(\delta_1 - \delta_2)}, \quad u = \frac{v}{b} = u_i = \frac{v_i}{b_i}. \quad (7)$$

The CHV-mixing rule [22] is a correction of the HVOS expression in Eq. (6) by weakening the influence of the term $x_i \ln(b/b_i)$

$$\frac{a}{bRT} = \sum x_i \frac{a_i}{b_i RT} + \frac{1-\lambda}{C} \sum x_i \ln \frac{b}{b_i} + \frac{A_\infty^E}{CRT}; \quad (8)$$

for both mixing rules the ratio u is unity at the infinitive pressure limit.

The G_0^E -mixing rules MHV1 [23] and PSRK [24] yield quite similar expression

$$\frac{a}{bRT} = \sum x_i \frac{a_i}{b_i RT} + \frac{1}{C} \sum x_i \ln \frac{b}{b_i} + \frac{G_0^E}{CRT}, \quad (9)$$

but they differ in the reference pressure p_0 chosen for the connection of the EOS and the activity coefficient model, resulting in different values for the ratio u

MHV1: $p_0 = 0 \rightarrow u = 1.235$; PSRK: $p_0 = 1 \text{ atm} \rightarrow u = 1.1$

The LCVm mixing rule [25] uses no reference pressure as it empirically combines the G_0^E -mixing rule MHV1 and the G_∞^E -mixing rule proposed by Huron and Vidal [26]

$$\frac{a}{bRT} = \sum x_i \frac{a_i}{b_i RT} + \frac{G^E}{RT} \left[\frac{\lambda}{C(u=1)} - \frac{1-\lambda}{C^{\text{MHV1}}} \right] + \frac{1-\lambda}{C^{\text{MHV1}}} \sum x_i \ln \frac{b}{b_i}. \quad (10)$$

The G^E -models (ACM) used in the G^E -mixing rules are the UNIQUAC and the NRTL model, cited for example in [27]. We used the original formulation of the interaction parameters (NRTL_3 and UNIQUAC_2) and temperature dependent parameters

$$\text{NRTL}_5: \tau_{ij}(T) = \frac{\Delta g_{ij} + \Delta g_{ij}^* T}{RT}; \quad \text{UNIQUAC}_6: \Delta u_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2 \quad (11)$$

with the attached number to the ACM according to the number of adjustable parameters. In order to achieve reasonable results for the saturation densities, we applied the volume translation proposed by Chou and Prausnitz [28] for the SRK and by Mathias et al. [29] for the PR equation of state

$$v_{\text{trans}} = v + s + f_c \frac{\eta}{\eta + d}, \quad d = \frac{-v^2}{RT_0} \left(\frac{\partial p}{\partial v} \right)_T; \quad (12)$$

f_c is the translation at the critical point, $\eta^{\text{SRK}} = 0.35$ [28] and $\eta^{\text{PR}} = 0.41$ [29]. We used a constant value for s as well as a temperature dependent volume correction [29] with

$$s = s_1 + s_2 \frac{T_c}{T}. \quad (13)$$

The relevant parameters for the mixture were determined by using linear mixing rules

$$s = \sum x_i s_i, \quad v_c = \sum x_i v_{ci}, \quad \frac{T_c}{p_c} = \sum x_i \frac{T_{ci}}{p_{ci}}. \quad (14)$$

Table 4: Averaged deviations of calculated pressure Δp (%) for the VLE and VLLE and of the determined compositions $\Delta x'_{N_2}$ (mol/mol) of the VLLE using SRK and PR EOS with different mixing rules and different ACM for the G^E -mixing rules.

mixing rule	+ACM	VLE	PR-EOS			SRK-EOS			
		Δp	Δp	$\Delta x'_{N_2}^{L1}$	$\Delta x'_{N_2}^{L2}$	Δp	Δp	$\Delta x'_{N_2}^{L1}$	$\Delta x'_{N_2}^{L2}$
vdW1		3.99	0.96	0.025	0.033	4.39	0.93	0.010	0.032
vdW2		2.24	1.29	0.055	0.019	2.30	1.05	0.045	0.015
MKP		2.60	1.35	0.059	0.023	2.46	1.11	0.054	0.017
TBCC		2.77	1.96	0.020	0.056	3.03	1.89	0.013	0.053
HVOS	+ NRTL_3	5.28	1.25	0.105	0.025	4.21	1.17	0.096	0.020
CHV		4.74	1.37	0.099	0.026	3.74	1.17	0.085	0.019
MHV1		5.60	1.24	0.109	0.024	4.42	1.06	0.097	0.019
PSRK		5.70	1.62	0.113	0.052	4.61	1.25	0.092	0.034
LCVM		4.96	1.27	0.107	0.026	3.89	1.17	0.091	0.020
HVOS	+ NRTL_5	2.15	1.21	0.033	0.017	2.23	1.06	0.037	0.014
CHV		2.10	1.22	0.038	0.017	2.19	1.03	0.034	0.014
MHV1		2.14	1.26	0.030	0.014	2.25	1.06	0.036	0.014
PSRK		2.26	1.40	0.035	0.028	2.27	1.13	0.036	0.018
LCVM		2.13	1.26	0.043	0.018	2.21	1.03	0.029	0.013
HVOS	+ UNIQUAC_2	5.21	1.06	0.163	0.024	4.44	0.56	0.169	0.024
CHV		5.05	0.66	0.172	0.029	4.23	0.55	0.167	0.023
MHV1		6.76	0.08	0.312	0.028	5.82	0.11	0.341	0.017
PSRK		6.48	1.07	0.067	0.017	4.24	1.39	0.016	0.041
LCVM		5.14	0.47	0.220	0.034	3.66	0.94	0.107	0.016
HVOS	+ UNIQUAC_6	1.64	0.95	0.024	0.016	1.81	0.92	0.026	0.020
CHV		1.51	0.93	0.021	0.018	1.55	0.96	0.016	0.024
MHV1		1.54	1.01	0.020	0.012	1.43	0.96	0.006	0.024
PSRK		1.73	1.11	0.027	0.012	1.79	0.98	0.030	0.013
LCVM		1.34	0.94	0.007	0.021	1.57	0.95	0.023	0.016

4. Results and Discussion

The binary interaction parameters in each mixing rules or G^E -mixing rule + ACM combination were calculated using a least squares optimization algorithm. The objective function involved the deviation between calculated vapor pressures of the VLE and experimental data [4-17, this work] covering a temperature range from 115 to 290 K. The adjusted binary interaction parameters are available from the authors on inquiry. The averaged deviations of the different models for the calculated vapor pressure of the VLE are listed in Table 4. We neglected the errors for the vapor phase composition completely as it consists of nearly pure nitrogen over a wide range of conditions. The CEOS with the classical vdW1-mixing rule yield Δp of about 4% due to increasing deviations with decreasing temperatures. The use of a second interaction parameter in

vdW2 already enables a more balanced prediction of the pressures over the whole temperature range resulting in a remarkable reduction of the average deviation. The performance of the composition dependent mixing rules are quite similar and do not offer any further advantage to the vdW2-mixing rule. The results of the G^E -mixing rules depend significantly on the ACM involved. The combinations with the NRTL_3 or UNIQUAC_2 model without temperature dependent interaction parameters yield a rather poor description of the VLE whereas NRTL_5 or UNIQUAC_6 give excellent results. The use of NRTL_3 or UNIQUAC_2 reveals slight differences in the performance of the different G^E -mixing rules showing some advantages of the CHV- and the LCVM-mixing rules. That leads to the assumption that the weakening of the $x_i \ln(b/b_i)$ term to avoid a double counting of the molecular sizes may be relevant for nitrogen-alkane systems. This advantage of both mixing rules is nearly offset when temperature depending interaction parameters are applied in the ACM. In this case are the results of the different G^E -mixing rules very similar and all superior to those of the vdW2 or composition dependent mixing rules. The best results for the description of the VLE are obtained by employing the UNIQUAC_6 model in the G^E -mixing rules as it uses the highest number of adjustable parameters. The comparison of both CEOS shows no significant differences between them, just slight advantages for the SRK EOS with composition dependent and G^E -mixing rules with temperature independent ACM. In case of the G^E -mixing rules is the advantage of the SRK EOS completely offset when temperature dependent interaction parameters are used in the ACM.

Regarding the prediction of the VLLE [12,13] it can be seen from Table 4 that all mixing rules yield good results for the pressure p_{VLLE} , the shortcomings of the models are revealed by their results for the composition of the two liquid phases in equilibrium. Surprisingly both, vdW2 and the composition dependent mixing rules do not improve the results of vdW1. According to the aforementioned results for the VLE the G^E -mixing rules with NRTL_5 or UNIQUAC_6 offer the best prediction of the VLLE whereas their combinations with NRTL_3 and especially UNIQUAC_2 are inferior to all other models. However, it has to be mentioned that no mixing rule gives a good description of the lighter liquid phase (L2) as the errors are from the same order of magnitude as its ethane concentration.

To investigate the description of the saturation densities we employed first a volume translation (VT) with a constant s determined by Luther [30] ($s_{\text{ethane}} = -1.644 \text{ cm}^3/\text{mol}$, $s_{\text{N}_2} = 0.530 \text{ cm}^3/\text{mol}$ for SRK; $s_{\text{ethane}} = 4.870 \text{ cm}^3/\text{mol}$, $s_{\text{N}_2} = 4.452 \text{ cm}^3/\text{mol}$ for PR).

The results listed in Table 5 show that the inaccurate prediction of the saturation liquid densities by the CEOS can largely be eliminated by this. In case of the PR EOS are the results getting worse at low temperatures due to larger deviations for the calculation of the liquid densities of the pure ethane. For this CEOS a temperature dependent volume translation (2VT, Eq. (13)) for ethane with $s_1 = 7.984 \text{ cm}^3/\text{mol}$ and $s_2 = -1.868 \text{ cm}^3/\text{mol}$ can lead to better results for the description of the liquid densities of the mixture. Neither the use of a temperature dependent volume translation for nitrogen nor for the SRK EOS yield a further improvement of the results shown in Table 5. It also demonstrates that the choice of the mixing rule does not significantly affects the results for the densities.

Table 5: Influence of the volume translation on the deviations of calculated saturation densities $\Delta\rho'$, $\Delta\rho''$ (%) using SRK and PR EOS with different mixing rules and G^E -mixing rule + ACM combinations. Experimental data: [11,14] and this work.

mixing rule	+ ACM	PR						SRK			
		without VT		VT		2VT		without VT		VT	
		$\Delta\rho'$	$\Delta\rho''$	$\Delta\rho'$	$\Delta\rho''$	$\Delta\rho'$	$\Delta\rho''$	$\Delta\rho'$	$\Delta\rho''$	$\Delta\rho'$	$\Delta\rho''$
vdW1		6.19	3.57	1.20	2.80	0.81	2.82	5.51	1.72	1.13	1.91
vdW2		5.62	4.14	1.30	3.37	0.95	3.38	6.26	1.76	1.79	2.13
MKP		6.24	3.87	1.11	3.10	0.79	3.11	5.56	1.73	1.16	2.03
TBCC		6.03	4.07	1.19	3.30	0.70	3.31	5.74	1.77	1.29	2.09
HVOS	+ NRTL_3	6.41	3.76	0.99	2.98	0.86	2.99	5.37	1.79	1.07	2.01
CHV		6.41	3.77	1.04	2.99	0.87	3.00	5.42	1.78	1.08	2.03
MHV1		6.43	3.74	0.98	2.96	0.87	2.97	5.36	1.79	1.07	2.01
PSRK		6.51	3.78	1.08	3.00	0.91	3.00	5.34	1.79	1.08	2.03
LCVM		6.39	3.79	1.00	3.01	0.86	3.02	5.40	1.78	1.08	2.02
HVOS	+ NRTL_5	6.13	4.02	1.12	3.25	0.73	3.26	5.65	1.74	1.23	2.06
CHV		6.15	4.01	1.10	3.24	0.75	3.25	5.65	1.75	1.22	2.07
MHV1		6.13	4.01	1.12	3.24	0.74	3.25	5.66	1.75	1.23	2.07
PSRK		6.13	4.12	1.13	3.34	0.73	3.35	5.64	1.77	1.21	2.14
LCVM		6.16	4.00	1.11	3.23	0.75	3.24	5.66	1.75	1.23	2.07
HVOS + UNIQUAC_2		6.46	3.59	1.01	2.92	1.02	2.93	5.42	1.73	1.22	2.00
CHV		6.47	3.75	1.03	2.97	1.04	2.97	5.44	1.72	1.24	2.00
MHV1		6.78	3.86	1.12	3.09	1.29	3.08	5.32	1.76	1.40	2.05
PSRK		6.46	3.70	0.94	2.93	1.04	2.94	5.42	1.72	1.18	2.02
LCVM		6.52	3.78	1.07	3.01	1.08	3.01	5.52	1.73	1.17	1.98
HVOS + UNIQUAC_6		6.05	4.09	1.07	3.32	0.75	3.33	5.70	1.77	1.22	2.12
CHV		6.05	4.07	1.09	3.29	0.74	3.31	5.76	1.85	1.28	2.02
MHV1		6.04	4.09	1.09	3.32	0.74	3.33	5.70	1.76	1.21	2.08
PSRK		6.04	4.20	1.09	3.42	0.75	3.43	5.70	1.77	1.22	2.14
LCVM		6.03	4.07	1.13	3.29	0.74	3.31	5.71	1.76	1.23	2.09

5. Conclusion

Based on reported experimental data and new measurements including saturated densities we investigated the performance of different mixing rules for CEOS for the description of the VLE, VLLE and saturation densities in the system nitrogen-ethane. The use of a second interaction parameter in the vdW2 already yields an improvement compared to the one parameter version. But for a more accurate reproduction of the complex phase behaviour G^E -mixing rules with temperature dependent parameters in the ACM are needed. However, the description of the saturation densities is mainly influenced by the volume translation but not by the mixing rule.

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